Cl^- (perhaps due to the ease of oxidation of Br^- as opposed to Cl^-). The $Br\cdot$ or $Cl\cdot$ thus produced can react rapidly with Cr^{2+} to yield $CrBr^{2+}$ and $CrCl^{2+}$, respectively. However, despite the scavenging ability of $Br\cdot$ by Cr^{2+},[2] the yield of $CrBr^{2+}$ is not increased over that for $CrCl^{2+}$ in Cl^- media. Another possibility for the product dependence upon Cl^- and Br^- is that these anions may offer a more favorable path for reduction of the nitrosyl with production of CrX^{2+} and decreasing amounts of Cr dimer.

In the absence of Cl^- or Br^-, how can virtually all the Cr be converted to dimer? In high acid, the results dictate a mechanistic sequence which results in the attack of one molecule of Cr^{2+} upon a molecule of $CrNO^{2+}$ in the rate-determining step, followed by a faster, further attack of another molecule of Cr^{2+} (concerted or stepwise) upon the activated complex (or its product) leading ultimately to the production of 1.5 molecules of the Cr dimer and a molecule of NH_3OH^+

$$Cr^{2+} + CrNO^{2+} \xrightarrow{\text{slow}} [Cr^{2+}, CrNO^{2+}]^{\ddagger}$$

$$Cr^{2+} + [Cr^{2+}, CrNO^{2+}]^{\ddagger} \xrightarrow{\text{fast}} 1.5(\text{Cr dimer}) + NH_3OH^+$$

The difficulty in constructing a mechanism for this reaction lies with the fact that the Cr dimer [not trimer[19] (λ_m 426, 580 nm and ϵ 31.4, 19.7 M^{-1} cm^{-1}, respectively)] is produced, and only 4-5% Cr^{3+} is produced. In addition, the stoichiometry dictates two molecules of Cr^{2+} per molecule of $CrNO^{2+}$. If Cr^{2+} had reduced the ligand in a simultaneous 2e-reduction step, one would have expected $^1/_3$ Cr^{3+} and Cr^{IV}; and the Cr^{IV} would then react with Cr^{2+} to produce $^2/_3$ Cr dimer. This is clearly not the case in our reaction. Thus, we can only suggest that Cr^{2+} attacks the $CrNO^{2+}$ producing some species which then reacts further with Cr^{2+} to produce Cr dimer. The abbreviated mechanism above is only meant to account for the kinetics. We cannot arrive at a complete mechanism which accounts for all the observed results. The implication at this point is that there may be an alternative route to the production of Cr dimer (other than the often quoted reaction $Cr^{2+} + Cr^{IV} \rightarrow$ Cr dimer). The complication here may be with the fact that we are reducing a coordinated ligand, nitrosyl, which is capable of undergoing *successive* reduction.[27] Reductions of coordinated nitrosyls have received little attention[28] in the past, and this work suggests that we may need to proceed with caution before drawing parallels to other ligand systems.

It is important to note that neither $CrNH_3{}^{3+}$ nor free $NH_4{}^+$ (in significant yields) was produced in this reaction. The reaction of Cr^{2+} with free NH_3OH^+ proceeds with a rate of 1.4×10^{-2} M^{-1} sec^{-1} at 25°, $\mu = 1.3$. Therefore, the further reduction of NH_3OH^+ by Cr^{2+} in our reaction does not compete successfully with the Cr^{2+} reduction of $CrNO^{2+}$.

Registry No. $Cr(H_2O)_6{}^{2+}$, 20574-26-9; NO, 10102-43-9; $Cr(H_2O)_5NO^{2+}$, 14951-34-9.

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[27] Presented at the 163rd National Meeting of the American Chemical Society, Boston, Mass., April 1972.

[28] Presented at the American Chemical Society Symposium on the Activation of Small Molecules by Transition Metals, Buffalo, N. Y., June 1972.

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Reduction of Vanadium Tetrachloride by Trimethylamine and Dimethylaminodichloroborane[1a]

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Investigation of the reduction of VCl_4 by methylamino moieties has been carried out. Trimethylamine results in the formation of dimethylmethyleneammonium chloride $(CH_3)_2N{=}CH_2{}^+Cl^-$, whereas dimethylaminodichloroborane, $(CH_3)_2NBCl_2$, affords the stabilized neutral imine $CH_3N{=}CH_2\cdot BCl_3$ and dimethylamine-boron trichloride, $(CH_3)_2NH\cdot BCl_3$. Reaction mechanisms are suggested for both reductions.

Reduction of $TiCl_4$, $TiBr_4$, and VCl_4 by $B_2[N(CH_3)_2]_4$ has been investigated in considerable detail. Titanium tetrachloride results in the formation of a binuclear Ti(III) species and the oxidation product $ClB[N(CH_3)_2]_2$ whereas $TiBr_4$ affords $\{B_2Br_2[N(CH_3)_2]_2\cdot TiBr_3\}_2$.[2,3] From the reaction stoichiometry associated with the reduction of $TiBr_4$ it was apparent that the B-B bond was not the reducing agent. Also, it is recognized that $N(CH_3)_3$ will reduce $TiCl_4$ and VCl_4; however, the oxidation product has not been identified.[4] During the investigation of the reduction of VCl_4 by $B_2[N(CH_3)_2]_4$ it became apparent that both B-B bonds and amino groups were serving as reducing agents.[5] In order to understand this very complicated chemical system it became necessary to investigate the manner in which methylamino moieties function as reducing agents for vanadium(IV) halides because the oxidation products of $B_2[N(CH_3)_2]_4$, $ClB[N(CH_3)_2]_2$, and $Cl_2B[N(CH_3)_2]_2$ are potential amine-type reducing agents. In order further to simplify the investigation, the reduction by $N(CH_3)_3$ was first explored.

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Results and Discussion

Trimethylamine Reduction of VCl_4. Treatment of VCl_4 with $N(CH_3)_3$ was investigated under various reaction conditions including order or reactant addition, influence of solvent, and effect of reaction temperature. Quantitative reduction takes place when VCl_4 is condensed onto excess liquid $N(CH_3)_3$ and allowed to warm slowly from −122 to +25°. These specific reaction conditions result in the redox chemical transformation summarized by eq 1.

$$2VCl_4 + 7N(CH_3)_3 \rightarrow 2VCl_3{\cdot}2N(CH_3)_3 + (CH_3)_3NH^+Cl^- + (CH_3)_2NCH_2N(CH_3)_3{}^+Cl^- \quad (1)$$

This reaction is substantiated on the basis of the experimentally determined reactant ratios and the amount of $VCl_3{\cdot}2N(CH_3)_3$ formed. Bis(trimethylamine)-vanadium(III) chloride was separated from the chloride salts, eq 1, by extraction with liquid $N(CH_3)_3$ and subsequently recrystallized. Characterization is based on an exact match of its ir spectrum with published data and ir data associated with another sample obtained from treatment of VCl_3 with $N(CH_3)_3$.[6] The $N(CH_3)_3$-insoluble residue contains $(CH_3)_3NH^+Cl^-$ as determined by comparison of the residue ir spectrum, Figure 1a, with that of $(CH_3)_3NH^+Cl^-$, Figure 1b, *i.e.*, coincident strong bands at 3005, 2950, 2615, 2511, 1481, 1409, 1258, and 988 cm^{-1}. (The respective data are recorded in the Experimental Section.) Complete removal of $VCl_3{\cdot}2N(CH_3)_3$ from this material is ensured based on the absence of a strong band at 506 cm^{-1}.

The first oxidation product of $N(CH_3)_3$ is the intermediate $(CH_3)_2N{=}CH_2{}^+$ which reacts with excess $N(CH_3)_3$ to afford $(CH_3)_2NCH_2N(CH_3)_3{}^+Cl^-$. This latter species was not isolated but is suggested to be one of several intermediates. Reduction of VCl_4 with a deficiency of $N(CH_3)_3$ [$VCl_4{:}N(CH_3)_3 = 1{:}1.5$] was carried out and the ir spectrum of the product mixture, Figure 1c, clearly indicates the presence of $\nu(C{=}N)$ at 1696 cm^{-1} and $\nu(H_2C)$ at 3120 cm^{-1}. For the sake of comparison the spectrum of $(CH_3)_2N{=}CH_2{}^+Cl^-$ is reproduced in Figure 1d with $\nu(C{=}N)$ at 1678 cm^{-1} and $\nu(H_2C)$ at 3080 cm^{-1}.[7] The published ir assignments for $(CH_3)_2N{=}CH_2{}^+I^-$, at 1682 and 3115 cm^{-1}, respectively, also verify these assignments.[8] Reaction of $(CH_3)_2N{=}CH_2{}^+$ with additional $N(CH_3)_3$ takes place as evidenced by loss of the $\nu(C{=}N)$, Figure 1a, to afford $(CH_3)_2NCH_2N(CH_3)_3{}^+Cl^-$, eq 1. Previous reports concerning the reaction of $(CH_3)_2N{=}CH_2{}^+Cl^-$ with amines are somewhat in conflict because $N(CH_3)_3$ is reported to afford the adduct $(CH_3)_2NCH_2N(CH_3)_3{}^+Cl^-$ while deprotonation is reported with $N(C_2H_5)_3$ to afford $(C_2H_5)_3NH^+Cl^-$ and volatile amines.[9,10] In an independent experiment, we have observed $(CH_3)_2N{=}CH_2{}^+Cl^-$ to undergo dehydrochloration when treated with $N(CH_3)_3$. This conclusion is based on the formation of $(CH_3)_3NH^+Cl^-$ which was identified by ir spectroscopy. We suggest, as have others, that the product from this deprotonation is an oligomer of $(CH_3)_2NCH$.[10]

Dichlorodimethylaminoborane Reduction of VCl_4. Treatment of VCl_4 with dimethylaminodichloroborane is described by eq 2. The boron-containing products were separated from

$$2VCl_4 + 2Cl_2BN(CH_3)_2 \rightarrow 2VCl_3 + CH_3N{=}CH_2{\cdot}BCl_3 + (CH_3)_2NH{\cdot}BCl_3 \quad (2)$$

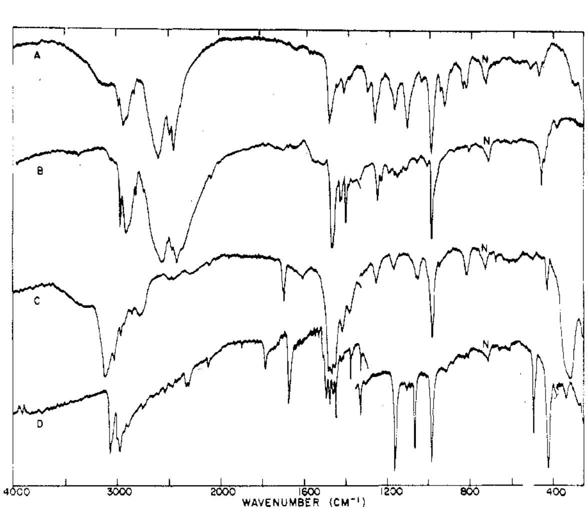

Figure 1. Infrared spectra: A, products from reaction ratio $N(CH_3)_3{:}VCl_4 = 3.5{:}1$; B, $(CH_3)_3NH^+Cl^-$; C, products from reaction ratio $N(CH_3)_3{:}VCl_4 = 1.5{:}1$; D, $(CH_3)_2N{=}CH_2{}^+Cl^-$.

VCl_3 by extraction with CH_2Cl_2, and the VCl_3 was characterized by its ir spectrum; the strong, broad $\nu(V{-}Cl)$ absorption at 295 cm^{-1} is the only feature of the spectrum.[11] The ir spectrum of the CH_2Cl_2-soluble fraction is shown in Figure 2a while those for $(CH_3)_2NH{\cdot}BCl_3$ and $[Cl_2BN(CH_3)_2]_2$ appear in Figure 2b and 2c, respectively. The presence of $(CH_3)_2NH{\cdot}BCl_3$ as a reaction product, eq 2, is confirmed by comparison of the ir spectra, Figure 2a and 2b; for example, there are coincident bands at 3184, 2962, 1374, 1337, 1148, 1143, 1135, 1003, 896, 831, 807, 506, 281, and 268 cm^{-1}. It should be noted that these ir bands are not associated with $[Cl_2BN(CH_3)_2]_2$. Only a small amount of $[(CH_3)_2NBCl_2]_2$ (either from incomplete reaction, eq 2, or a dehydrochlorination product of $(CH_3)_2NHBCl_3$)) is present based on the weak (normally very strong) ir bands at 1234, 1207, 1029, 934, 540, and 408 cm^{-1}.

Diagnostic ir bands associated with $CH_3N{=}CH_2{\cdot}BCl_3$, *i.e.*, not present in $(CH_3)_2NH{\cdot}BCl_3$ or $[Cl_2BN(CH_3)_2]_2$, are found at 1669, 1073, and 950 cm^{-1}. The imine vibration $\nu(C{=}N)$ at 1669 cm^{-1} compares favorably with the published assignments of the boron trifluoride-imine adducts: $C_6H_5(H)C{=}NCH_3{\cdot}BF_3$, 1712 cm^{-1}; $C_6H_5(H)C{=}NC_6H_5{\cdot}BF_3$, 1673 cm^{-1}.[12] The ir bands at 1073 and 950 cm^{-1} are also vibrations of the imine base and are assigned to $\nu(NC)$ and $\rho_w(CH_2)$, respectively.[13] Other distinctive ir bands are expected for $CH_3N{=}CH_2{\cdot}BCl_3$ but these are masked by the presence of the other adduct $(CH_3)_2NH{\cdot}BCl_3$. The $\nu(CH_2)$ absorptions are buried under $\nu(NH)$ and are found at 3184 cm^{-1}; $\delta(CH_2)$ is expected in the 1450-1400-cm^{-1} region but assignment is not possible. Absorptions of the BCl_3 unit ν_{as}, ν_s, δ_{as}, and δ_s of $CH_3N{=}CH_2{\cdot}BCl_3$ are expected to be buried under the corresponding vibrations of $(CH_3)_2NH{\cdot}BCl_3$. The adduct mixture absorbs strongly at 830, 807, 780, 753, and 733 cm^{-1} while $(CH_3)_2NH{\cdot}BCl_3$ has absorptions at 831, 807, 778, 748, and 737 cm^{-1}. Previous workers have assigned absorptions in the spectrum of $(CH_3)_3N{\cdot}BCl_3$: $\nu_s(CN)$, 833 cm^{-1}; $\nu_{as}(B^{10}Cl_3)$ and $\nu(BN)$, 786 and 755 cm^{-1}; $\nu_{as}(B^{11}Cl_3)$, 746 cm^{-1}.[14] The lack of other strong absorptions in the BCl re-

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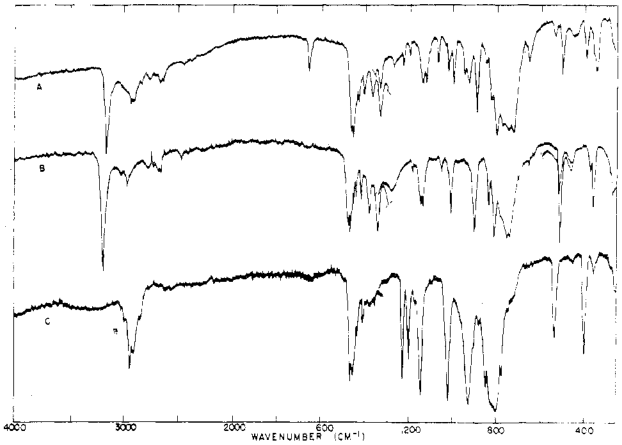

Figure 2. Infrared spectra: A, $CH_3N{=}CH_2 \cdot BCl_3$ and $(CH_3)_2NH \cdot BCl_3$; B, $(CH_3)_2NH \cdot BCl_3$; C, $[Cl_2BN(CH_3)_2]_2$.

gion, 800–1000 cm^{-1}, indicates the presence of only four-coordinate BCl moieties.

In an attempt to separate and/or isolate stable derivatives of the BCl_3 adducts, eq 2, several experiments were carried out. The mixture was treated separately with pyridine (py) and trimethylamine. In neither case could $py \cdot BCl_3$ or $(CH_3)_3N \cdot BCl_3$ be isolated; ir data, associated with both reaction products, indicated dehydrochlorination takes place. In an effort to characterize further the imine-boron trichloride adduct $CH_3N{=}CH_2 \cdot BCl_3$, a Diels-Alder reaction with butadiene was attempted. Only partial dimerization of the butadiene took place as evidenced by isolation of cyclooctadiene: ν(CH) 3040 and 3090 cm^{-1}, ν(C=C) 1650 cm^{-1}, and ρ(CH) 748 cm^{-1}; parent mass *m/e* 108. The ir spectrum of the nonvolatile reaction residue from the diene reaction was identical with that of the starting mixture, *i.e.*, $CH_3N{=}CH_2 \cdot BCl_3$ and $(CH_3)_2NH \cdot BCl_3$. Controlled pyrolysis of the adduct mixture at 48° *in vacuo* affords a mixture of white solid and clear oil; the ir spectrum of this mixture is identical with that of one of the starting material. Attempts to obtain ^1H nmr data on the BCl_3 adduct mixture were unsuccessful most likely due to rapid relaxation attributed to trace quantities of V(IV) species.

Bis(dimethylamino)chloroborane Reduction of VCl_4. The reduction of VCl_4 by bis(dimethylamino)chloroborane, $ClB[N(CH_3)_2]$, is complex because of the additional amino group. Various reaction conditions were investigated including solvent, order of addition, mole ratio of reagents, and reaction temperature. The only characterized product of this system is a small amount of $Cl_2BN(CH_3)_2$ produced by metathetical ligand exchange between VCl and $BN(CH_3)$ moieties. Exchange reactions are common for dimethylamino moieties particularly when the species are capable of bridging or chelating.[15]

All of the reacted VCl_4 and essentially all of the borane used is found as a nonvolatile insoluble amorphous solid. Oxidation of an NCH_3 moiety occurs forming C=N and V(3+) species, however this redox reaction is not quantitative. The bases for these conclusions are the presence of ν(C=N) absorptions between 1690 and 1699 cm^{-1} for all solids investigated and the combined analytical and magnetic vanadium data indicating the approximate distribution of oxidation states, 47% V(III) and 53% V(IV). No tractable vanadium complexes could be isolated from this chemical system.

Mechanism of Methylamino Reduction of VCl_4. A series of reactions may be written, which account for the reduction of VCl_4 by NCH_3 moieties, involving either ionic or radical species. A radical mechanism is favored because it incorporates several known chemical facts. Vanadium tetrachloride is more readily reduced by $N(CH_3)_3$ than is $TiCl_4$, *i.e.*, reduction of $TiCl_4$ takes place at 25° but not at 0° whereas VCl_4 undergoes reduction at −111°. The relative stability of $TiCl_4$ and VCl_4, to amine reduction, parallels the relative thermodynamic stability of $TiCl_4$ and VCl_4 toward decomposition affording $TiCl_3$ and VCl_3, respectively, in addition to $Cl \cdot (Cl_2)$.[16] The favored radical mechanism incorporates Cl· elimination, and the ease of reduction of VCl_4 *vs.* $TiCl_4$ is understandable based on the relative thermodynamic stability of the parent tetrachlorides. An ionic mechanism must involve elimination of Cl^- and it is difficult to explain the observed relative rates of reduction based on known chemical facts. Finally, the reduction of VCl_4 by $Cl_2BN(CH_3)_2$ takes place under homogeneous reaction conditions until precipitation of VCl_3. If an ionic mechanism were operable, one would expect precipitation of ionic intermediate species in the relatively nonpolar solvent CH_2Cl_2.

Reduction of VCl_4 by $N(CH_3)_3$. The initial reaction of VCl_4 with $N(CH_3)_3$ is considered adduct formation, eq 3, followed by elimination of Cl· to form $(CH_3)_3NVCl_3$, eq 4.

$$N(CH_3)_3 + VCl_4 \rightarrow (CH_3)_3N \cdot VCl_4 \quad (3)$$

$$(CH_3)_3N \cdot VCl_4 \rightarrow (CH_3)_3N \cdot VCl_3 + Cl\cdot \quad (4)$$

The driving force for Cl· elimination from "VCl_4," at −111°, is stabilization of the V^{3+} product species $VCl_3 \cdot N(CH_3)_3$, eq 4. Equation 5 represents H· abstraction from $N(CH_3)_3$ by Cl·; this reaction parallels the known reaction of $(CH_3)_3N$ with NOCl to afford $(CH_3)_3NH^+Cl^-$.[17] The eliminated HCl, eq 5, is expected to react with the excess $N(CH_3)_3$ present affording $(CH_3)_3NH^+Cl^-$, eq 6. The methylene radical, eq 5,

$$N(CH_3)_3 + Cl\cdot \rightarrow (CH_3)_2NCH_2\cdot + HCl \quad (5)$$

$$N(CH_3)_3 + HCl \rightarrow (CH_3)_3NH^+Cl^- \quad (6)$$

may react by H· abstraction with $N(CH_3)_3$, eq 7, which results in no net chemical change. Cl· abstraction, eq 8, results in the formation of the observed intermediate dimethylmethyleneammonium chloride, $(CH_3)_2NCH_2{}^+Cl^-$, where the Cl^- is actually part of a larger unidentified anionic species. Evidence for this latter conclusion is associated with the small shift of the ν(C=N) frequency for $(CH_3)_2N{=}CH_2{}^+$ species as a function of the anion size.[7,8,18]

$$(CH_3)_2NCH_2\cdot + N(CH_3)_3 \rightarrow (CH_3)_2NCH_3 + (CH_3)_2NCH_2\cdot \quad (7)$$

$$(CH_3)_2NCH_2\cdot + (CH_3)_3N \cdot VCl_4 \rightarrow (CH_3)_3N \cdot VCl_3 + (CH_3)_2NCH_2{}^+Cl^- \quad (8)$$

In the presence of excess $N(CH_3)_3$ this latter species undergoes deprotonation as reported in this work. Further complex formation of $(CH_3)_3N \cdot VCl_3$ takes place to afford the isolated bis adduct, eq 9.

$$(CH_3)_3N \cdot VCl_3 + N(CH_3)_3 \rightarrow VCl_3 \cdot 2N(CH_3)_3 \quad (9)$$

Reduction of VCl_4 by $(CH_3)_2NBCl_2$. In a manner analogous to the $N(CH_3)_3$ reduction of VCl_4, $(CH_3)_2NBCl_2$ reduction of VCl_4 is initiated by adduct formation, eq 10. The

$$(CH_3)_2NBCl_2 + VCl_4 \rightarrow Cl_2BN(CH_3)_2 \cdot VCl_4 \quad (10)$$

slower rate of reduction of VCl_4 by $(CH_3)_2NBCl_2$, compared

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with the $N(CH_3)_3$ reaction, is rationalized based on the decreased base strength of the borane. For example, titanium tetrachloride does not form a complex with $Cl_2BN(CH_3)_2$; hence the absence of reduction of $TiCl_4$ by $Cl_2BN(CH_3)_2$ is not surprising.[19] In the case of VCl_4, the formation of the simple adduct, eq 10, is suggested to be followed by induced $Cl\cdot$ and VCl_3 formation, eq 11. As in the case of $N(CH_3)_3$

$$Cl_2BN(CH_3)_2\cdot VCl_4 \rightarrow (CH_3)_2NBCl_2 + VCl_3 + Cl\cdot \qquad (11)$$

reduction, abstraction of $H\cdot$ from $(CH_3)_2NBCl_2$ by $Cl\cdot$ takes place but in this case producing a methylene radical, eq 12.

$$(CH_3)_2NBCl_2 + Cl\cdot \rightarrow Cl_2B(CH_3)NCH_2\cdot + HCl \qquad (12)$$

The methylene radical may abstract $H\cdot$ from $(CH_3)_2NBCl_2$ in a "nonreaction" similar to eq 7 or it may function as a reducing agent toward VCl_4 with elimination of Cl^- which reacts with the generated cations affording the isolated neutral imine complex $CH_3N{=}CH_2\cdot BCl_3$, eq 13. Finally the production of

$$Cl_2B(CH_3)NCH_2\cdot + VCl_4 \rightarrow CH_3N{=}CH_2\cdot BCl_3 + VCl_3 \qquad (13)$$

the other isolated BCl_3 adduct, $(CH_3)_2NH\cdot BCl_3$, is explained by combination of HCl, eq 12, and $(CH_3)_2NBCl_2$ as represented by eq 14.

$$(CH_3)_2NBCl_2 + HCl \rightarrow (CH_3)_2NH\cdot BCl_3 \qquad (14)$$

The reaction mechanisms proposed, in conjunction with the NCH_3 moiety reductions of VCl_4, have greatly aided in the development of an understanding of how $CH_2[N(CH_3)_2]_2$ is produced from the treatment of VCl_4 with $B_2[N(CH_3)_2]_4$.[5]

Experimental Section

General Techniques. Reagents and products handled in this investigation react readily with trace amounts of oxygen and water. Consequently all manipulations were carried out with vigorous exclusion of air and moisture. Conventional vacuum-line techniques were employed, and the line was equipped with Teflon stopcocks obtained from the Fisher and Porter Co., Warminster, Pa., or Kontes Glass Co., Vineland, N. J.[20,21] Reactor connections to the vacuum system were *via* O-ring joints, 9-mm i.d., obtained from Fusion, Inc., Rosemond, Ill., employing Viton A or Buna N O rings. Nonvolatile and low volatile materials (less than 0.2 Torr vapor tension at ambient temperature) were manipulated in a metal drybox, Kewanee Scientific Corp., Adrain, Mich. The atmosphere in this box was maintained at a positive pressure with high-purity gaseous nitrogen (99.996% by volume) from Liquid Carbonic Corp. This was passed through two columns, 2 ft × 1-in. diameter, containing granulated phosphorus pentoxide. The static atmosphere in the box was scavanged for transpirated oxygen and moisture by an open pan of sodium–potassium alloy which was skimmed constantly. Masses of samples, both volatile and nonvolatile, were determined with a Sartorius single-pan balance, Model 2602, precision ±0.3 mg over its entire range. Millimolar amounts of volatile materials were expanded into calibrated sections of the vacuum line and determined using *PVT* data.

Spectroscopic Techniques. Gas-phase infrared studies were performed using a 10-cm gas cell equipped with KBr or CsBr windows. Infrared spectra of solids were obtained as mulls. Fluorolube, grade S-20, obtained from Hooker Chemical Co., Niagara Falls, N. Y., and Nujol, USP mineral oil (both dried with molecular sieve, Linde 4A), were used as mulling agents in the spectral regions 4000–1330 and 1380–250 cm^{-1}, respectively. A Perkin-Elmer Model 457 grating spectrophotometer calibrated using the 1601.4-cm^{-1} absorption of poly(styrene) was used for all infrared measurements.

Analytical Methods. Samples were sealed in weighing vials and solid NaOH or KOH was placed in the neck of the Teflon stopcock and the system was connected to the vacuum line. Water was condensed onto the samples and refluxed, washing the base into the hydrolysis mixture. The sample solutions were made acidic with H_2SO_4 and taken off the vacuum line, transferred to a volumetric flask, and analyzed using standard wet chemical techniques.

Vanadium was determined as V_2O_5 using the Turner method.[22] Interference tests with boric acid and dimethylammonium chloride indicated that this method is accurate in the systems investigated. Boron, nitrogen (volatile base), and chloride were analyzed as previously described.[19] Chloride aliquots were taken directly from the stock solution with no pretreatment because addition of V(III), V(IV), $B(OH)_3$, or $HN(CH_3)_2$ produced no interference in standardization titrations. Concerning boron analyses, interference studies showed that the presence of V^{3+} species could not be tolerated for accurate analyses; consequently all V was oxidized to the IV or V state with basic peroxide followed by heating in acid to destroy excess H_2O_2.

Reagents. Unless otherwise stated cylinder gases were obtained from the Matheson Co., Inc., Joliet, Ill. Solvents were dried with CaH_2 prior to purification by trap to trap fractional condensation.

Trimethylamine, obtained from the Matheson Co., Inc., Joliet, Ill., contained *ca.* 3.5% $(HN(CH_3)_2$ as an impurity. The $N(CH_3)_3$ was purified by condensing it in *ca.* 50-ml (liquid) portions on pulverized $LiAlH_4$. This mixture was maintained at −78° for 2 days with constant stirring followed by 1 day at 0°. Volatile material from this process was transferred to a thick-walled Pyrex storage vessel equipped with a Teflon stopcock and maintained at 25° until needed. Prior to use the amine was fractionated several times through two −78° traps in series. The vapor tension of the $N(CH_3)_3$ passing through the −78° traps was 75.5 Torr at −45.2°, lit.[23] 76 Torr.

Vanadium tetrachloride was obtained from Stauffer Chemical Co., Weston, Mich. A gas-phase infrared spectrum of the purchased material indicated the presence of $VOCl_3$: absorptions at 1035 cm^{-1} assigned to $\nu(V{=}O)$ and at 509 cm^{-1} assigned to $\nu(V{-}Cl)$ in $VOCl_3$.[24] Hydrolysis followed by Cl and V analyses are consistent with this sample of VCl_4 containing 3.5% $VOCl_3$. Fractional distillation of the VCl_4 was accomplished with a partial pressure of 119 Torr He with a 2-ft vacuum-jacketed distillation column. The VCl_4 fraction was collected, 90.5–91.5°, while $VOCl_3$ was collected at *ca.* 70°; VCl_4P at 91° (119 Torr) and $VOCl_3P$ at 68° (119 Torr).[25] The VCl_4 thus purified contained 73.45 ± 0.07% Cl; the calculated amount from VCl_4 is 73.57% Cl. The gas-phase ir spectrum of this material indicated a very weak shoulder at 506 cm^{-1}. Infrared data of VCl_4: $\nu(V{-}Cl)$ at 489 cm^{-1} in the gas phase; lit.[26] 475 cm^{-1} in solution.

Butadiene. Butadiene was purified by fractional condensation through traps maintained at −95 and −196°. The −196° fraction had a vapor tension of 111 Torr at −45.2°; lit.[27] 111 Torr.

Lithium Dimethylamide. *n*-BuLi in hexane, 418 mmol, 164 ml (2.55 mmol/ml), was diluted with *ca.* 100 ml of hexane. The mixture was thermostated at 0° and 420 mmol, 18.92 g, of $HN(CH_3)_2$ was added in the vapor phase. The total pressure of the system was not allowed to exceed 700 Torr; addition required *ca.* 1 hr. Vigorous stirring was maintained throughout the addition process and for 1 hr after warming to 25°. All volatile material was removed by maintaining the snowy white solid at 10^{-5} Torr for 8 hr.

Bis(dimethylamino)chloroborane, $ClB[N(CH_3)_2]_2$, and dichlorodimethylaminoborane, $Cl_2BN(CH_3)_2$ were prepared by treatment of a pentane solution of BCl_3 with a pentane slurry of $LiN(CH_3)_2$. A typical reaction is described. BCl_3, 30.4 mmol, 3.56 g, in *ca.* 50 ml of C_5H_{12} was treated with a slurry of 55.0 mmol, 2.81 g, of $LiN(CH_3)_2$ in C_5H_{12}. Volatile material was removed immediately and stored for 1 week to permit dimerization of $Cl_2BN(CH_3)_2$. Fractionation of this mixture through a −45° trap separated $ClB[N(CH_3)_2]$ (P = 1.3 Torr at 0°) from C_5H_{12}, P = 14 Torr at −45°.[28] The nonvolatile material was pure $[Cl_2BN(CH_3)_2]_2$ and characterized by its ir spectrum, Figure 2C, with bands at 3140 (w), 3006 (w), 2960 (s), 2929 (s), 2868 (w), 1474 (s), 1462 (s), 1439 (m), 1413 (w), 1388 (w, br), 1234 (s), 1207 (s), 1172 (w, sh), 1155 (s), 1029 (s), 934 (s), 858 (s), 818 (s, br), 786 (m, sh), 540 (s), 408 (s), 361 (m), 283 (m, sh), and 268 (m) cm^{-1}.[29]

Bis(dimethylamino)methane, $H_2C[N(CH_3)_2]_2$, was prepared by treatment of a decane slurry of $LiN(CH_3)_2$ with methylene chloride, CH_2Cl_2. A two-necked 500-ml bulb was filled with 274 mmol, 14.00 g, of $LiN(CH_3)_2$ and *ca.* 150 ml of $C_{10}H_{22}$. Methylene chloride, 140 mmol, 8.5 ml, was added to this slurry in the vapor phase and the re-

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sultant mixture stirred for 2 days. The contents were then refluxed at 85° and 40 Torr He pressure while all material which passed through a cold water condenser trap was collected in a −195° trap. This was found to be a mixture of CH_2Cl_2, $HN(CH_3)_2$, and $H_2C[N(CH_3)_2]_2$. Treatment with $LiAlH_4$ removed all $HN(CH_3)_2$ and fractionation through a −45° trap removed CH_2Cl_2. The contents of the −45° trap was characterized by its ir spectrum, mass spectra (parent mass at *m/e* 102), and vapor tension P_{0° = 23.6 Torr, lit.[30] 23.6 Torr.

Trimethylamine hydrochloride was prepared by the gas-phase reaction with dry HCl. Ir data: 3008 (s), 2960 (s, br), 2858 (w, sh), 2620 (vs, br), 2521 (s, br), 2481 (vs, br), 2418 (s, br), 1480 (vs), 1475 (sh), 1441 (m), 1434 (s), 1413 (s), 1259 (m), 1243 (w), 1205 (w, br), 1180 (w), 1164 (w), 1121 (w, br), 1068 (w), 1018 (w), 988 (vs), 181 (w), 721 (m), 466 (m), 450 (m, sh), 390 (w) cm^{-1} (Figure 1B).[31]

Vanadium trichloride was obtained by the decomposition of VCl_4 at 150° with a partial pressure of 1 atm of He. The Cl_2 liberated was trapped by constant exposure to a closed-end U tube cooled to 196°. The dark red-brown solid, VCl_3, was characterized by its infrared spectrum: 1010 (vw), 365 (sh), 291 (vs, br) cm^{-1}.[11]

Bis(trimethylamine)trichlorovanadium(III). $VCl_3 \cdot 2N(CH_3)_3$ was prepared by treatment of 1.04 mmol (0.1646 g) of VCl_3 with liquid $N(CH_3)_3$. Initially there was little change in the purple color of the VCl_3 but with continued contact time the purple-rose color of the bis complex developed. After 3 days the complex was dissolved in benzene to effect separation from unreacted VCl_3. A total of 0.1673 g, 0.608 mmol, was obtained. Characterization was accomplished by comparison of its infrared spectrum with the published data in addition to its elemental analysis.[6] *Anal.* Calcd: Cl, 38.60; N, 10.17. Found: Cl, 38.5; N, 10.2.

Reactions of Vanadium Tetrachloride with Trimethylamine. The sealed-ampoule method for preparing bis(trimethylamine)-vanadium(III) chloride, $VCl_3 \cdot 2N(CH_3)_3$, I, described by earlier workers was attempted with varying degrees of success.[32] Vanadium tetrachloride and $N(CH_3)_3$ were condensed into thick-walled Pyrex tubes which were then sealed *in vacuo*. The systems were maintained at ambient temperature for 1–2 days. Benzene was used to extract soluble I from the black, red, red-brown, brown, and white solids. The method was modified so that VCl_4 could be added in the vapor phase to a large excess of $N(CH_3)_3$ in a tared bulb. The amine was maintained at −111° and stirred vigorously; the first color observed in the vapor-liquid reaction was bright red. However, a solid formed which became almost immediately more purplish and then finally changed to a red-brown mudlike material as the mixture became more concentrated in VCl_4. This mixture was warmed to room temperature and stirred for 1 day. No change in color either of the red-brown solid or the red-purple solution was observed during this time period. Pure $N(CH_3)_3$ was the only volatile component of the reaction system and was characterized by its ir spectrum, mass spectrum and vapor tension, P_{-45° = 77 Torr, lit.[23] 76 Torr. As the solvent was removed, the solid became more red-pink.

Measurements of VCl_4 and $N(CH_3)_3$ used and recovered and the mass of nonvolatile solid formed were found to be internally consistent. In this manner 6.69 mmol of VCl_4, 1.2891 g, added to 89.5 mmol of $N(CH_3)_3$, 5.2882 g, produced 2.5775 g of nonvolatile solid and 67.7 mmol, 4.0028 g, of residual $N(CH_3)_3$. In a similar reaction, 7.85 mmol of VCl_4 combined with 131.6 mmol of $N(CH_3)_3$, producing the nonvolatile red-brown solid and leaving 104.8 mmol of $N(CH_3)_3$. Compound I was extracted from these solids with $N(CH_3)_3$; 6.92 mmol was obtained from the latter reaction while in a larger scale reaction 35.0 mmol of VCl_4 produced 32.9 mmol of I. No additional amine was consumed in these extractions. The infrared spectra of I contains bands at 3013 (s), 2982 (s), 2932 (s), 2905 (s), 2880 (m), 2855 (s), 2824 (m), 2796 (ms), 2463 (w), 1478 (vs), 1458 (vs), 1404 (vs), 1238 (m), 1103 (ms), 987 (vs), 812 (vs), 506 (s), 442 (s), 410 (vs), 289 (m), and 252 (m) cm^{-1}.[6,32]

After extraction of the red-brown solid with $N(CH_3)_3$ there remained a nonvolatile white solid(s) which contained ir absorptions at 3005 (m), 2950 (ms), 2920 (sh), 2840 (w), 2615 (vs, br), 2515 (m, sh), 2511 (m), 2470 (vs), 1481 (s), 1441 (w), 1409 (w), 1258 (s), 1162 (m), 1102 (s), 1030 (w), 988 (vs), 940 (w), 920 (m), 830 (m), 815 (m), and 462 (m) cm^{-1} (Figure 1A).

Stepwise reaction of VCl_4 with $N(CH_3)_3$ was accomplished using an inert solvent. A pentane solution of VCl_4, 14.38 mmol, 2.7695 g, was rapidly added in the vapor phase to a pentane solution of $N(CH_3)_3$, 21.2 mmol, 1.2517 g, at −111°. The red solid that formed initially appeared similar to that observed in the previous neat reactions. This solid also became more purple after a short period of time. Pentane was removed from the mixture as it warmed from −111°; when dry, the solid is light red. No mass calculations were carried out, but the volatile phase was colorless indicating the absence of any V species and exhibited a vapor tension close to that of pure pentane, P_{0° = 186, lit.[28] 183 Torr. No I was isolated from this system when extracted with pure pentane. Ir data: 3120 (vs), 3023 (s), 2983 (m), 2925 (sh), 2860 (m), 2790 (m, br), 1696 (m), 1606 (w, br), 1500 (w, sh), 1478 (s), 1465 (s), 1450 (s), 1412 (ms), 1379 (m), 1250 (mw), 1160 (w), 1050 (mw), 996 (sh), 980 (s), 975 (sh), 940 (w), 811 (mw), 719 (Nujol), 690 (w, br), 600 (w, br), 490 (w), 423 (m), 320 (vs, br), and 255 (ms) cm^{-1} (Figure 1C).

Preparation of Dimethylmethyleneammonium Chloride. According to the literature method, 9.11 mmol, 0.9302 g, of $CH_2[N(CH_3)_2]_2$ was diluted with 1.81 g of CH_3CN in a 20-ml weighing vial.[9] Acetyl chloride, 7.41 mmol, 0.5815 g, was admitted slowly to this clear colorless solution with constant stirring. Volatile components were removed from the white nonvolatile solid *in vacuo*. The total amount of residual nonvolatile white solid was 0.6992 g. This solid has ir absorptions at 3080 (m), 3013 (sh), 2988 (m), 2910 (sh, br), 1893 (w), 1678 (m), 1511 (sh), 1498 (m), 1491 (m), 1464 (m), 1450 (ms), 1381 (m), 1333 (m), 1172 (vs), 1078 (s), 992 (vs), 921 (w), 720 (w), 500 (s), 430 (s), 345 (w), and 280 (w, sh) cm^{-1} (Figure 1D). Sublimation of this solid at 100° *in vacuo* produced a white crystalline substance whose infrared spectrum was identical with that indicated above. No further purification was attempted.

Reaction of Dimethylmethyleneammonium Chloride with Trimethylamine. (a) According to the literature method, a slurry of 3.86 mmol of $(CH_3)_2N{=}CH_2{}^+Cl^-$, 0.3613 g, in 3.90 g of CH_3CN was treated with gaseous $N(CH_3)_3$, 25.4 mmol, 1.5058 g.[9] The methyleneammonium salt was only sparingly soluble in CH_3CN, but with addition of $N(CH_3)_3$ the white solid dissolved to give a slightly yellow solution. As more amine was added, a white precipitate formed but subsequently dissolved during removal of volatile materials after completion of the reaction. Removal of additional volatile material resulted in the solution becoming more yellowish and finally a solid again precipitated. The total amount of nonvolatile solid was 0.5055 g. The ir spectrum of this white solid indicated extensive $(CH_3)_3NH^+Cl^-$ formation had taken place. Ir data: 3160 (m, br), 3005 (vs), 2960 (vs, br), 2808 (vs), 2629 (vs, br), 2521 (s), 2494 (s), 1780 (w), 1642 (w), 1492 (s, sh), 1486 (vs), 1450 (s), 1414 (s), 1371 (m), 1351 (m), 1294 (m), 1270 (w), 1250 (m), 1211 (m), 1156 (ms), 1140 (m), 1110 (m), 1089 (s), 1069 (s), 990 (s), 948 (s), 887 (w), 849 (ms), 818 (ms), 748 (w), 719 (Nujol), 680 (m), 532 (w), 492 (w), 462 (w), and 429 (mw) cm^{-1}.

(b) An attempt to prepare dimethylaminomethylenetrimethylammonium chloride, $(CH_3)_2NCH_2N(CH_3)_3{}^+Cl^-$, was made by stopping the reaction in the soluble state. A slurry of 2.09 mmol, 0.1953 g, of $(CH_3)_2N{=}CH_2{}^+Cl^-$, in CH_3CN, was treated with 2.69 mmol, 0.1590 g, of $N(CH_3)_3$. The slight excess of amine was necessary to dissolve the last traces of methyleneammonium salt. The volatile materials were removed, *in vacuo*, leaving 0.301 g of nonvolatile white solid. The ir spectrum of this material is essentially identical with that obtained during the reaction with excess amine, the only difference being a weak absorption at 1678 cm^{-1} indicating the presence of trace amounts of unreacted $(CH_3)_2N{=}CH_2{}^+Cl^-$.

(c) Dimethylmethyleneammonium chloride, 191.0 mg, 2.04 mmol, was treated with $N(CH_3)_3(g)$, 55.9 Torr, for 12 hr. After no further decrease in the pressure of the reaction system, 31.4 Torr, a mass measurement indicated 40.1 mg, 0.678 mmol, of amine was absorbed. An ir spectrum of this material indicates the presence of unreacted $(CH_3)_2N{=}CH_2{}^+Cl^-$ and the presence of $(CH_3)_3NH^+Cl^-$. A sample of $N(CH_3)_3$, 1.2 mmol, was added to the residual white solid. (After the infrared spectrum was taken, 206.1 mg of solid remained.) The total pressure in this gas-phase reaction was estimated to be *ca.* 450 Torr. After maintaining this closed system for 24 hr an additional 20.8 mg of $N(CH_3)_3$ was absorbed. The volatile phase from this reaction appeared to be substantially pure $N(CH_3)_3$ by ir. The solid was next treated with liquid $N(CH_3)_3$ for 7 hr. An additional 40.9 mg of amine reacted bringing the reactants stoichiometry to 1:0.7:4. An ir spectrum of this material indicated extensive deprotonation had occurred.

Reaction of Vanadium Tetrachloride with Dimethylaminodichloroborane. (a) Treatment of VCl_4, 0.7451 g (3.88 mmol), with $(CH_3)_2NBCl_2$, 0.9076 g (7.22 mmol), dissolved in CH_2Cl_2, for 4 days at 25° resulted in the slow precipitation of a red-brown solid. Removal of all volatile materials afforded 1.3003 g of nonvolatile residue. Fractionation and subsequent ir analysis indicated the presence of

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only CH_2Cl_2 and $(CH_3)_2NBCl_2$ in the volatile phase. Mole ratio VCl_4:$(CH_3)_2NBCl_2$ reacted is 1:1.14. Subsequent filtration of the residue, *in vacuo*, with CH_2Cl_2 afforded insoluble VCl_3, 0.6173 g (3.92 mmol), and 0.6830 g of white solid which has ir absorptions at 3184 (s), 2960 (m), 2940 (m, sh), 2860 (w), 2790 (w), 2695 (w), 2660 (w), 1664 (m), 1470 (s, sh), 1463 (s), 1447 (s), 1434 (m), 1409 (m), 1372 (m), 1335 (m), 1276 (w), 1231 (w), 1205 (w), 1158 (s), 1145 (s), 1138 (s), 1128 (w, sh), 1072 (m), 1028 (m), 1001 (m), 950 (m), 930 (m), 897 (s), 852 (w), 830 (m, sh), 807 (s), 780 (s), 753 (s), 733 (s), 658 (m), 537 (w), 505 (m), 457 (w), 400 (m), 366 (m, sh), 348 (m), 310 (w), 281 (sh), and 270 (m) cm^{-1}, Figure 2A.

(b) Treatment of VCl_4, 1.9485 g (10.10 mmol), with $(CH_3)_2$-$NBCl_2$, 0.5978 g (4.76 mmol), dissolved in CH_2Cl_2 for 6 days at 25° afforded 0.9696 g of a red-brown solid. Work-up, as in (a) above, yielded VCl_3, 0.3453 g (2.19 mmol), and 0.6243 g of soluble material. Infrared analysis of this soluble fraction indicated the presence of $[Cl_2BN(CH_3)_2]_2$ in addition to the absorptions found in (a) above. In both (a) and (b) above the adduct mixture was light yellow. A spot test for V with chromatropic acid confirmed its presence in trace quantities.[33]

Attempted Separations of $CH_3N{=}CH_2{\cdot}BCl_3$ and $(CH_3)_2NH{\cdot}BCl_3$. (a) Treatment of the $CH_3N{=}CH_2{\cdot}BCl_3$–$(CH_3)_2NH{\cdot}BCl_3$ mixture, *ca.* 150 mg, with 1 ml of liquid pyridine (py) resulted in a faintly red solution in addition to the presence of white crystalline material. Pyridine and CH_3Cl, the only characterized (ir) volatile material, were removed *in vacuo*. An ir spectrum of the nonvolatile product consisted of several broad (~500 cm^{-1}) absorptions; one of these, 2390–2780 cm^{-1}, indicated extensive dehydrochlorination.

(b) Treatment of the $CH_3N{=}CH_2{\cdot}BCl_3$–$(CH_3)_2NH{\cdot}BCl_3$ mixture with both gaseous and liquid $(CH_3)_3N$ resulted in the formation of a solid similar to that obtained in the pyridine reaction. Volatile products were not investigated; the nonvolatile material was an intractable white gumlike solid with an ir spectrum exhibiting strong absorptions in the 2400–2800-cm^{-1} region indicating the presence of N-H· · ·Cl due to dehydrochlorination.

(c) Approximately 300 mg of adduct mixture was treated with *ca.* 800 Torr of gaseous butadiene. The system was cooled to 0° and maintained with vigorous stirring for 3 hr. Volatile material was removed *in vacuo* and passed through traps maintained at −95 and −196°; pure butadiene, contained in the −196° trap, was characterized by its ir spectrum and vapor tension. The contents of the −95° trap was tenatively characterized as cyclooctadiene by its ir spectrum [ν(CH) 3040, 3090 cm^{-1}, ν(C=C) 1650 cm^{-1}, ρ(CH) 748 cm^{-1}] and its mass spectrum; the parent mass was found at *m/e* 108. The P + 1 mass at 109 was 8.% of the parent; the predicted P + 1 mass is 5.7% of the parent based on the isotopic abundances of ^{13}C and ^2H.[34] The ir spectrum of the nonvolatile reaction residue was identical with that of the starting material. The adduct mixture (10% by volume) did not afford a ^1H nmr signal. Furthermore, nmr signals were lacking for samples known (by ir) to contain significant amounts of $[Cl_2BN(CH_3)_2]_2$; see (b) above.

Fractional sublimation of the mixture $CH_3N{=}CH_2{\cdot}BCl_3$–$(CH_3)_2$-$NH{\cdot}BCl_3$ (150 mg total) was carried out in 3° increments between 25 and 48° at 10^{-7} Torr. Sublimation with decomposition took place at 48° as evidenced by condensation of a white solid mixed with a clear liquid. An ir spectrum of this material is identical with that of the original adduct mixture, *i.e.*, $CH_3N{=}CH_2{\cdot}BCl_3$–$(CH_3)_2NH{\cdot}BCl_3$. No volatile components of this pyrolysis were detected.

Reactions of Vanadium Tetrachloride with Bis(dimethylamino)-chloroborane. Investigation of this chemical system included neat reactions as well as solvent variation. In addition this reaction was studied from −78 to 25° and the reactant mole ratios were varied as well as the order of addition. It was not possible to isolate and characterize a vanadium complex from any of the reaction systems investigated. The following is a typical example of the reactions carried out. A solution of $ClB[N(CH_3)_2]_2$, 5.14 mmol, 0.6919 g, in pentane was treated with 5.10 mmol, 0.9818 g, of VCl_4. The borane solution was maintained at −78° while care was taken not to cool the reaction vessel above the solution level. As is the case with $N(CH_3)_3$ reductions, if liquid VCl_4 reacted with the Lewis base, a dark red-brown material was formed which was quite different from the material produced in the gas–liquid system. A brown solid was immediately formed with addition of VCl_4(g); this solid was insoluble in the pentane–$ClB[N(CH_3)_2]_2$ solution. Volatile materials were removed, *in vacuo*, and found to contain small amounts of $Cl_2BN(CH_3)_2$ monomer in addition to excess $ClB[N(CH_3)_2]_2$ as characterized by their ir spectra. The nonvolatile phases consisted of a tan solid and a minor (mass-wise) red-brown solid. The tan solid could be separated from the red-brown material because the latter clung to the walls of the reaction vessel.

The tan solid was insoluble in C_5H_{12}, C_6H_6, CCl_4, and CH_2Cl_2 and reacted with tetrahydrofuran to give a red solution. Magnetic data indicate $\chi_g = 6.88 \times 10^{-6}$ cgsu. Analysis of this solid indicates the following composition: 50.6% Cl, 15.8% V, 2.8% B, and 8.11% N. Infrared data (tan solid): 3134 (vs), 2974 (s), 2934 (m), 2884 (m), 2713 (m), 1698 (w), 1657 (w), 1472 (vs), 1447 (s), 1416 (m), 1186 (w), 1147 (w), 1127 (w), 1081 (w), 1058 (w), 1010 (m), 1006 (m), 957 (w), 907 (m), 852 (m), 842 (m), 815 (w), 787 (w), 728 (w), 539 (w), 513 (w), 470 (w), 457 (w), 440 (w), 327 (vs) cm^{-1}. Slow pyrolysis, *in vacuo*, to 74° resulted in no observable change in the tan solid. Continued heating to 87° resulted in the solid's becoming dull white with sublimation of a small amount of brown material. At 130° a sufficient quantity of $(CH_3)_2NH_2{}^+Cl^-$ formed to characterize it by ir. A mixture of HCl, CH_3Cl, and a trace of an unidentified gas is produced with continued pyrolysis to 280°. These components were characterized by their respective ir and mass spectra. The tan solid is also amorphous as an X-ray powder photograph exposed for 12 hr to Cu Kα radiation does not indicate any crystal structure.

Preparation of $(CH_3)_2NH{\cdot}BCl_3$. Thirty milliliters of BCl_3(l) were transferred to a tared weighing vial and thermostated at −95° with stirring. Dimethylamine, 0.1559 g, 3.455 mmol, was slowly added to the BCl_3 immediately forming a white insoluble solid. Dimethylamine cannot be allowed to condense on the sides of the reaction vessel as this results in a nonhomogeneous product. Volatile materials were immediately removed as the bulb warmed slowly from −95 to +25°. At no time was the mixture allowed to warm and yet remain in contact with BCl_3. The mass of nonvolatile solid was 0.4995 g while that predicted is 0.5614 g. This latter number assumes (1) all the amine remains in the reaction vessel and (2) the only product is the simple adduct. This first assumption is wrong because BCl_3 removed from the reaction bulb contained a quantity of white solid estimated to be between 20 and 40 mg. The melting point with decomposition of $(CH_3)_2NH{\cdot}BCl_3$ was 122–129°. Ir data: 3184 (vs), 2962 (w), 2789 (w), 2749 (w), 2687 (w), 2684 (w), 1470 (ms), 1461 (ms), 1448 (w), 1434 (w), 1410 (m), 1374 (s), 1335 (s), 1270 (m), 1143 (ms), 1148 (s), 1130 (s), 1044 (w), 1003 (vs), 896 (vs), 831 (ms), 807 (vs), 778 (sh), 748 (s, br), 737 (s, br), 506 (ms), 457 (w), 369 (w, sh), 353 (ms), 269 (m) cm^{-1}.

Registry No. VCl_4, 7632-51-1; $N(CH_3)_3$, 75-50-3; $VCl_3{\cdot}2N(CH_3)_3$, 20538-61-8; $(CH_3)_3NH^+Cl^-$, 593-81-7; $(CH_3)_2NCH_2N(CH_3)_3{}^+Cl^-$, 16133-14-5; $(CH_3)_2N{=}CH_2{}^+Cl^-$, 30354-18-8; $[Cl_2BN(CH_3)_2]_2$, 25928-65-8; $CH_3N{=}CH_2{\cdot}BCl_3$, 38680-99-8; $(CH_3)_2NH{\cdot}BCl_3$, 13072-44-1; $CH_2CHCHCH_2$, 106-99-0; $ClB[N(CH_3)_2]$, 6562-41-0; BCl_3, 10294-34-5; $LiN(CH_3)_2$, 3585-33-9; CH_2Cl_2, 75-09-2; $H_2C[N(CH_3)_2]_2$, 51-80-9; $(CH_3)_2NH$, 124-40-3.

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